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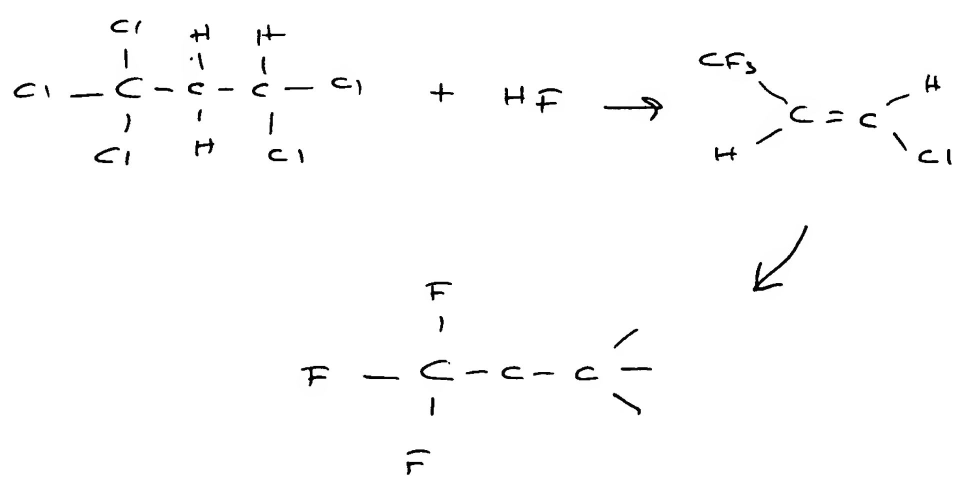
(54) **Synthesis of 1-chloro-3,3,3-trifluoropropene and 1,1,1,3,3-pentafluoropropane**

(57) 1,1,1,3,3- Pentafluoropropane ($CF_3CH_2CHF_3$) is manufactured by fluorination of 1,1,1,3,3-pentachloropropane ($CCl_3CH_2CHCl_2$) with anhydrous hydrofluoric acid (HF). The reaction is carried out in two stages: the first, in the gas phase, provides essentially 1-chloro-3,3,3-trifluoropropene ($CF_3CH{=}CHCl$) and the second, in the liquid phase, makes it possible to convert the 1-chloro-3,3,3-trifluoropropene to 1,1,1,3,3-penta-fluoropropane.



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SYNTHESIS OF 1-CHLORO-3,3,3-TRIFLUOROPROPENE AND ITS FLUORINATION TO 1,1,1,3,3-PENTAFLUOROPROPANE

The present invention relates to the preparation of 1,1,1,3,3-pentafluoropropane (known in the trade under the name HFA 245fa) from 1,1,1,3,3-pentachloropropane (240fa).

Due to the effect on the stratospheric ozone layer of chlorofluorohydrocarbons (CFCs), which were conventionally used as refrigerants, aerosol propellants and foam-expansion agents, the production and the consumption of CFCs have been regulated and new products have had to be developed.

Research to find replacements for these compounds has been focused, firstly, on products containing hydrogen atoms (HCFCs) and then on products which contain no chlorine: hydrofluorocarbons (HFCs).

Among the latter, an increasing interest appears to be emerging in C_3 compounds (including HFA 245fa). For example, the use of 1,1,1,3,3-pentafluoropropane is mentioned in various patent specifications, in particular as foam-expansion agent (JP 5239251), as expansion agent, propellant gas and cleansing solvent for the electronics industry (DD 298419) and as heat-transfer fluid (JP 2272086).

Knunyants *et al.* (*Izvest. Akad. Nauk. S.S.S.R., Otdel. Khim. Nauk.* 1960, 1412-1418; C.A. 55: 349c and *Kinet. Katal.* 1967, *8(6)*, 1290-1299; C.A. 69:

3510n) describe the synthesis of 1,1,1,3,3-pentafluoropropan by catalytic hydrogenation of 1,1,3,3,3-pentafluoro-1-propene (CF_3-CH=CF_2) over catalysts based on palladium deposited on alumina. However, it is not easy to obtain the starting material and the authors clearly specify that they were confronted with problems of selectivity due to "substitution" reactions of the fluorine atoms by hydrogen atoms.

More recently, various patent specifications (US 2,942,036, EP 677,503, EP 611,744, EP 687,659, WO 94/29251, WO 94/29252, WO 95/4022 and WO 95/13256) have described the preparation of 1,1,1,3,3-pentafluoropropane by processes for the hydrogenolysis of chlorofluorinated propane derivatives, such as $CF_3CHClCF_2Cl$, $CF_3CCl_2CF_2Cl$, $CF_3CHClCHF_2$, $CF_3CCl_2CHF_2$ or $CF_3CH_2CF_2Cl$. Besides the fact that these hydrogenolysis reactions are not generally very selective, the disadvantage of these processes lies in the preparation of the chlorofluorinated starting material which requires a number of reaction stages.

EP 690,038 describes the preparation of HFA 245fa by liquid-phase fluorination of $CF_3CH_2CHCl_2$ and/or CF_2ClCH_2CHFCl. Although this fluorination gives good results, such a process is difficult to operate industrially and has little economic viability because of the difficulty of access of the starting materials, which were prepared by reaction of vinylidene fluoride (CF_2=CH_2) with dichlorofluoro-methane ($CHCl_2F$).

WO 96/1797 describes the preparation of HFA 245fa by liquid-phase reaction of 1,1,1,3,3-pentachloropropane with anhydrous hydrofluoric acid in the presence of a fluorination catalyst according to the reaction:

$$CCl_3CH_2CHCl_2 + 5\ HF \rightarrow CF_3CH_2CHF_2 + 5\ HCl$$

Because of the ready accessibility of the chlorinated derivative, such a fluorination process constitutes a real advance over the processes described previously. According to WO96/1797, the fluorination can be carried out under entirely conventional liquid-phase fluorination conditions in the presence of antimony chlorofluorides at approximately 135°C and with approximately 10 to 25% by weight of catalyst with respect to the organic materials. The yields indicated in the various examples are not, however, very good (57% for Example 1, 54% for Example 2 and 71% for Example 3) and, except for Example 1, where it is indicated that 11% of 244fa are formed, it is not possible to know the nature and the amount of the by-products formed.

Examination of this fluorination reaction in detail has now shown that relatively large amounts of by-products are systematically formed, these by-products being essentially products from the chlorination and/or coupling of the 240fa or of its

conversion products.

These products are less volatile than 245fa, accumulate in the reactor, cannot be recycled and correspondingly decrease the overall yield. The amounts of these heavy products formed during this fluorination very clearly depend on the operating conditions and increase as the reaction temperature increases and as the amounts of catalyst and/or of chlorine increase; they generally correspond to approximately 10 to 20% of the pentachloropropane charged. These heavy products are essentially C_6 olefinic or diolefinic products, the most important of which were able to be identified and correspond to the following empirical formulae:

$C_6H_4F_7Cl$

$C_6H_4F_6Cl_2$

$C_6H_3F_8Cl$

$C_6H_3F_6Cl_3$

$C_6H_2F_6Cl_2$

On continuing its studies relating to the preparation of HFA 245fa by fluorination of 240fa with anhydrous hydrofluoric acid, the Applicant Company has found that a gas-phase catalytic fluorination process makes it possible very readily to obtain complete conversion of 240fa. As the fluorination of the CCl_3- group is much easier than that of the $CHCl_2$- group, the fluorination products obtained during such a process all have a terminal CF_3- group. However, in contrast to what might have been expected, the major reaction

product is not HFA 245fa but 1-chloro-3,3,3-trifluoropropene:

$CF_3CH{=}CHCl$ 1233zd

The selectivities for the olefin 1233zd are generally much greater than 50% and can reach values as high as 90%. The other products from the gas-phase fluorination are:

$CF_3CH_2CHF_2$	245fa
CF_3CH_2CHFCl	244fa
$CF_3CH_2CHCl_2$	243fa
$CF_3CH{=}CHF$	1234ze

and only traces of other by-products are formed.

Under certain conditions, in particular with very high HF/240fa molar ratios, it had been possible to obtain relatively high selectivities for 245fa which can reach 30 to 40% and, by carrying out the fluorination at high temperature (300 - 350°C) and with high HF/240 molar ratios, the selectivities for the olefin 1234ze were able to reach approximately 15%. However, the olefin 1233zd always remains the major product. On account of the very similar volatilities of HFA 245fa (B.p. 15°C) and of the olefin 1233zd (B.p. 20.8°C), it is virtually impossible to separate these two products by simple distillation and it is therefore

impossible to recycle this 1233zd during a fluorination process intended for the manufacture of 245fa.

It has, in addition, been found that the olefin 1233zd and the other products which possibly accompany it and which result from the gas-phase fluorination (243fa, 244fa and 1234ze) can be converted to 245fa by a liquid-phase catalytic fluorination process. In contrast to the liquid-phase fluorination of 240fa, which, in addition to 245fa, results in numerous heavy by-products which decrease the yield, the liquid-phase fluorination of 1233zd and of the other products from the fluorination of 240fa which already contain a terminal CF_3 (243 fa, 244fa and 1234ze) is much cleaner and results in only traces of heavy products. The 243fa, 244fa and 1234ze can optionally be separated from the 1233zd and 245fa by distillation, before being charged to the liquid-phase fluorination, but such a separation is in no way necessary and there is every advantage in directly charging the crude product obtained during the gas-phase stage to the stage for the liquid-phase fluorination.

According to a first aspect of the present invention, there is provided a process for the manufacture of 245fa by fluorination of 240fa, which fluorination is carried out in two successive stages:

- the first fluorination stage is carried out in the gas phase and provides mainly 1233zd, possibly

accompanied by 243fa, 244fa, 245fa and 1234ze;

- the second fluorination stage is carried out in the liquid phase and makes it possible to convert the 1233zd and the products which possibly accompany it (243fa, 244fa and 1234ze) to 245fa.

According to further aspects of the invention, there are provided the individual stages. Thus the invention provides separately:

- the manufacture of 1233zd by gas-phase fluorination of 240fa;

- the manufacture of 245fa by liquid-phase fluorination of 1233zd.

The 1,1,1,3,3-pentachloropropane (240fa) used as starting material can be readily prepared in a single stage according to processes known per se by reaction of tetrachloromethane (CCl_4) with vinyl chloride (CH_2=CHCl), two widely available industrial products.

Gas-phase fluorination of 240fa

This gas-phase fluorination comprises treating, in the gas phase, a mixture of 240fa and hydrofluoric acid in the presence of a fluorination catalyst.

The fluorination catalysts to be used can be bulk catalysts or supported catalysts, the support stable in the reaction mixture being, for example, an active charcoal, aluminium fluoride or aluminium phosphate.

Mention may more particularly be made, among bulk catalysts, of chromium oxide prepared according to methods known to the person skilled in the art (sol-gel process, precipitation of the hydroxide from chromium salts, reduction of chromic anhydride, and the like). The derivatives of metals such as nickel, iron, manganese, cobalt or zinc can also be suitable, alone or in combination with chromium, in the form of bulk catalysts but also in the form of supported catalysts.

The supported catalysts can be employed in the form of balls, extrudates, pellets or even, if the reaction is carried out in a stationary bed, in the form of lumps. For the bulk catalysts, the pellet or ball form is generally preferred. When the reaction is carried out in a fluid bed, it is preferable to use a catalyst in the form of balls or extrudates.

Mention may be made, as non-limiting examples of catalysts, of:

- chromium oxide microbeads obtained by the sol-gel process as described in FR 2,501,062,
- catalysts containing chromium oxide deposited on active charcoal (US 4,474,895), on aluminium phosphate (EP 55 958) or on aluminium fluoride (US 4,579,974 and 4,579,976),
- mixed catalysts containing chromium oxide and nickel fluoride deposited on aluminium fluoride (EP 0,486,333),
- bulk catalysts based on nickel and chromium

oxides (EP 0,546,883),

- catalysts containing nickel fluoride deposited on fluorinated alumina.

These patent specifications, the contents of which are incorporated here by reference, fully describe the method of preparation of these catalysts and also their method of activation, that is to say of prior conversion of the catalyst into stable active species by fluorination by means of gaseous HF diluted with inert compounds (nitrogen) or air. During this activation, the metal oxides which act as active material (for example chromium oxide) or as support (for example alumina) can be partially or completely converted to the corresponding fluorides.

Preference is given to catalysts based on chromium oxide (bulk or supported) and to mixed catalysts containing chromium oxide and nickel fluoride.

The gas-phase catalytic treatment of 240fa with HF according to the invention is advantageously carried out at a temperature of between 140°C and 400°C. The minimum temperature does not depend solely on the reactivity of the 240fa but in particular on the need to keep the 240fa/HF reaction mixture gaseous and to prevent any condensation of this 240fa (B.p. 182°C). Another advantage in not operating at an excessively high temperature is not to deactivate the catalyst too rapidly. For this reason the reaction is preferably

carried out at a temperature of between 180°C and 350°C.

The pressure is not critical and the reaction is preferably carried out under a pressure of between atmospheric pressure and 1.5 MPa.

The contact time can vary within wide limits, for example from 0.5 to 100 seconds, but a contact time of between 2 and 30 seconds is preferred, this contact time being defined by the relationship:

$$ct = \frac{3600 \times V \times 273 \times P \times 10}{22.4 \times th \times (T+273)}$$

where	P	=	pressure in MPa
	ct	=	contact time in seconds
	th	=	throughput in mol/hour
	V	=	bulk catalyst volume, expressed in litres
	T	=	temperature of the reactor in degrees Celsius

The HF/240fa molar ratio can also vary within wide limits but it is generally preferable to operate with a molar ratio of between 5 and 30.

It may be advantageous, with certain catalysts and under certain conditions, to operate in the presence of a small amount of oxygen or of chlorine in order to improve the lifetime of the catalyst. The amount of oxygen or chlorine used, with respect to the 240fa feeding the reaction, can vary between 0.1 and 5

molar %. The oxygen or the chlorine can be introduced into the reaction region either alone or as a mixture with an inert material, such as nitrogen. The use of these two compounds is not without disadvantage for the selectivity of the reaction and, in order for it not to be excessively reduced, it is advantageous to use amounts of these catalyst deactivation inhibitors which are as low as possible.

The products of the reaction containing products from the fluorination of 240fa (243fa, 244fa, 245fa, 1233zd and 1234ze), unconverted HF and the HCl formed are treated according to methods known per se, that is to say by distillation and/or washing with water, in order to separate the HCl and optionally all or part of the unconverted HF. From an economic viewpoint, it is advantageous to separate by distillation all the HCl formed and to charge, in subsequent liquid-phase fluorination, the mixture of the fluorinated organic products formed and of the unconverted HF.

Liquid-phase fluorination of 1233zd

The liquid-phase fluorination of the 1233zd and optionally of the products which are liable to accompany it, is carried out in the presence of a fluorination catalyst.

The catalyst for this fluorination reaction with anhydrous hydrofluoric acid in the liquid phase may be chosen from derivatives of metals belonging to

the main groups IIIa, IVa and Va and to the sub-groups IVb, Vb and VIb. These metal compounds can be used alone or as a mixture. Use may more especially be made, among the elements selected from the columns of the Periodic Classification, of titanium, niobium, tantalum, molybdenum, boron, tin and antimony. The species containing antimony are particularly well suited. Use may be made, as metal derivative, of oxides, oxyhalides and halides. Halides are more particularly chosen, with a preference for chlorides, fluorides and chlorofluorides. Antimony pentachloride ($SbCl_5$) is especially well suited; its use results in a significant conversion of the products charged and in a high selectivity for 1,1,1,3,3-pentafluoropropane.

The amount of catalyst employed in this liquid-phase fluorination can vary within wide limits. There is generally used at least 0.005 mol of catalyst per mole of organic products to be fluorinated and but not more than 0.5 mol of catalyst per mole of organic products to be fluorinated. The amount of catalyst used is preferably from 0.02 mol to 0.25 mol of catalyst per mole of organic products to be fluorinated.

The liquid-phase fluorination according to the invention is implemented by heating the reactants and can be carried out batchwise or continuously. The reaction temperature is generally at least 50°C and it most often does not exceed 150°C. The reaction is preferably carried out at a temperature of 80°C to

140°C.

Under batchwise conditions, the reaction may be carried out in a closed reactor into which all the reactants are introduced at the beginning of the operation. The autogenous pressure increases with the progression of the reaction, to reach a maximum value. According to this process, the molar ratio of anhydrous hydrofluoric acid to 1233zd and the products which possibly accompany it is generally between 2 and 30 and more particularly between 3 and 15.

The reaction can also be carried out under batchwise conditions by introducing, at the beginning, all the reactants into a reactor surmounted by a column which enables the hydrochloric acid formed to be removed. The pressure is maintained at a constant value via a pressure regulator. The pressure is determined so that the bulk of the hydrochloric acid can be removed and that the bulk of the organic products remain in the liquid state in the reaction mixture. Depending on the temperature of the reaction mixture, the pressure is generally regulated at a value of between 5 and 30 bars.

Under continuous conditions, the reactants are steadily fed into the reaction mixture containing the catalyst. The reactor is advantageously surmounted by a column which makes possible the continuous removal of a portion or all of the light compounds generated during the reaction (hydrochloric acid and

1,1,1,3,3-pentafluoropropane) and the condensation of the heavier compounds (catalyst, hydrofluoric acid and intermediate chlorofluorinated products). The reaction pressure is maintained at a predetermined value by means of an appropriate regulating device. This value is defined, on the one hand, to make possible the separation of the hydrochloric acid by distillation and, on the other hand, to keep the reaction mixture in the liquid state; it thus varies as a function of the temperature of the reaction mixture. The reaction pressure is generally at least 5 bars but does not exceed 60 bars. The reaction pressure preferably lies between 10 and 40 bars. Pressures of between 12 and 30 bars have proved to be particularly advantageous.

The HFA 245fa can be separated from the reaction products by methods known per se and the unconverted hydrofluoric acid and the underfluorinated organic products can be recycled.

Would be 244fa + 243fa See p5

For the purpose of maintaining the activity of the catalyst, and in particular that of the antimony pentahalides, and to prevent deactivation by reduction to antimony trihalide, it is advantageous to carry out the fluorination in the presence of a small amount of chlorine. This addition of chlorine can be carried out continuously when the fluorination is carried out continuously and the amount of chlorine fed with the organic products to be fluorinated is in this case generally 0.005 to 0.05 mol of chlorine per mole of

organic products fed. When the fluorination is carried out batchwise, the chlorine can be introduced periodically.

The following Examples illustrate the invention without, however, limiting the scope thereof. In these examples, the percentages shown are understood to be in moles, except when otherwise indicated.

EXAMPLE 1

100 ml of a catalyst based on nickel fluoride and on chromium oxide deposited on aluminium fluoride were placed in an Inconel 600 tubular reactor with an internal diameter of 28 mm and a volume of 200 ml. The physicochemical characteristics of this catalyst, prepared as described in EP 0,486,333 and activated as a stationary bed with a nitrogen/HF mixture, are as follows:

- *Chemical composition (by weight)*:
  - fluorine : 58.6%
  - aluminium : 25.9%
  - nickel : 6.4%
  - chromium : 6.0%
- *Physical properties*:
  - apparent density (in bulk) : 0.85 g/ml
  - BET specific surface : 23 m^2/g
  - volume of the pores with a radius of between 4 nm

and 63 μm : 0.4 ml/g

specific surface of the pores with a radius greater than 4 nm : 23 m^2/g

After a final "in situ" activation of the catalyst using a gaseous nitrogen/HF mixture between 25°C and 250°C, the reactor was fed with a gaseous mixture composed of HF and of 240fa in proportions such that the HF/240fa molar ratio is 14. The pressure in the reactor was maintained at atmospheric pressure and the feed throughput of the 240fa + HF mixture was adjusted so as to have a contact time of 2 seconds.

The gases which emerge from the reactor are washed with water, dried over a calcium chloride bed and condensed in a dry ice trap at -78°C. The test was carried out in this way at 250°C for 48 hours and an appraisal was carried out for the last 24 hours of operation. During this period, 1450 g of 240fa were fed and 845 g of trapped products were recovered, these trapped products containing, according to chromatographic analyses and identifications by mass and NMR spectroscopy, the following proportions of products:

82%	1233zd, including 88% of trans isomer and 12% of cis isomer;
8.2%	1234ze, including 85% of trans isomer and 15% of cis isomer;
0.2%	243fa

0.6% 244fa

8.5% 245fa

The 240fa was completely converted and the overall yield of 1233zd + 1234ze + 243fa + 244fa + 245fa was 97.3%.

EXAMPLES 2 to 7

Various tests of the gas-phase fluorination of 240fa were carried out in the same reactor as Example 1 and with the same catalyst, the contact time, the temperature and the HF/240fa molar ratio being modified. All these tests were carried out for 18 hours and the reaction products were analyzed by gas-phase chromatography at the end of the test.

The operating conditions and the molar compositions of the products obtained appear in Table 1, in comparison with the test of Example 1.

These tests make it possible to observe that the conversion of 240fa is always quantitative. The 1233zd is always the major compound by a large margin. The amount of HFA 245fa increases as the temperature falls and as the HFA/240fa molar ratio increases; during the best test (Example 5), no more than 36% of 245fa is obtained.

TABLE 1

EXAMPLE	1	2	3	4	5	6	7
Temperature (°C)	250	250	300	350	250	250	250
Contact time (s)	2	12	12	12	6	12.1	12
HF/240fa molar ratio	14	14.7	14.7	14.1	28	9.8	5
Molar composition of the products obtained (%):							
1233zd	82	73.6	73.2	78.3	52.6	72.5	80.9
1234ze	8.2	5.1	14.2	15.5	9.7	6	4.7
243fa	0.2	0.2	<0.1	<0.1	<0.1	0.4	1.3
244fa	0.6	0.7	0.4	0.2	0.6	1.1	2.1
245fa	8.5	19.8	9.5	2.5	36	18.5	9.1
Various	0.5	0.6	2.6	3.5	1	1.5	1.9

EXAMPLES 8 to 12

Various tests of fluorination of 240fa were carried out in the same reactor as in Example 1 but containing 100 ml of a commercial bulk chromium oxide catalyst as 4.8 x 4.8 mm pellets which has been preactivated as a stationary bed using a nitrogen/HF mixture. The pressure was maintained at atmospheric pressure.

The physicochemical characteristics of this catalyst, after activation, are as follow:

- *Chemical composition (by weight)*:
  - fluorine : 20.0%
  - chromium : 56.3%

carbon : 3.5%

- oxygen : 20.2%

- *Physical properties*:
  - apparent density (in bulk) : 1.21 g/ml
  - BET specific surface : 124 m^2/g
  - volume of the pores with a radius of between 4 nm and 63 μm : 0.14 ml/g
  - specific surface of the pores with a radius greater than 4 nm : 42.3 m^2/g

The tests were carried out in a way entirely similar to Examples 1 to 7 and the operating conditions and the molar compositions of the products obtained are shown in Table 2.

As for Examples 1 to 7, it is found that the 1233zd is always the major product. The two catalysts give very similar results (see Examples 2 and 8). At low temperatures (150°C), the level of 245fa formed is very low and 1233zd is formed substantially exclusively.

TABLE 2

EXAMPLE	8	9	10	11	12
Temperature (°C)	250	200	180	150	150
Contact time (s)	11.7	5.3	5.3	5.8	19.3
HF/240fa molar ratio	14.8	14.5	14.9	14.7	14
Molar composition of the products obtained (%):					
1233zd	71.2	61.5	75.5	91.4	86.9
1234ze	4.8	2.1	1.1	0.8	1.9
243fa	0.2	0.4	0.6	0.7	0.3
244fa	0.7	1.4	1.9	2.9	2.1
245fa	20.6	34.2	20.6	3.9	7.3
Various	2.5	0.4	0.3	0.3	1.5

EXAMPLE 13

15 g of antimony pentachloride $SbCl_5$ (0.05 mol), 100 g of anhydrous hydrofluoric acid (5 mol) and 66 g of 1233zd (0.50 mol) were introduced successively into an 800 ml INOX 316L autoclave equipped with a pressure indicator, a thermometric probe, a bursting disc and a system for stirring with a magnetic bar.

The reactor was heated to 120°C and the pressure gradually increased to reach 42.5 bars. After 5 and a half hours, the reaction system was brought back to room temperature and a residual pressure of 14 bars was observed.

Analyses of the various phases collected gave the following results:

- degree of conversion of 1233zd: ≥ 99.9%
- selectivity for 1,1,1,3,3-pentafluoropropane: 85.6%
- selectivity for 244fa: 1.3%
- selectivity for 243fa: 12.4%

The major by-product was identified as being an olefinic compound of empirical formula $C_3HCl_2F_3$ (selectivity 0.7%).

EXAMPLE 14

38 g of antimony pentachloride (0.127 mol), 154 g of anhydrous hydrofluoric acid (7.7 mol) and 167 g of 1233zd (1.28 mol) were introduced successively into a 1000 ml INOX 316L autoclave equipped with a condenser (connected to a pressure indicator/regulator system), a pressure indicator, a thermometric probe, a bursting disc and a system for stirring with a magnetic bar.

Circulation of water (T = 20°C) was established in the condenser; the reactor was heated to 120°C and the pressure was regulated at 20 bars by removal of light compounds. After 5 and a half hours, the reaction system was brought back to room temperature; a residual pressure of 1.6 bars was observed.

Analyses of the various phases collected after complete degassing of the autoclave gave the following results:

- degree of conversion of 1233zd: ≥ 99.9%

- selectivity for 245fa: 92%
- selectivity for 244fa: 1%
- selectivity for 243fa: 6%

EXAMPLE 15

30 g of antimony pentachloride (0.1 mol), 200 g of anhydrous hydrofluoric acid (10 mol) and 130 g of the reaction mixture of Example 1 were introduced successively into the same equipment as that of Example 14, the reaction mixture of Example 1 containing:

82%	1233zd
8.2%	1234ze
0.2%	243fa
0.6%	244fa
8.5%	245fa

that is to say one mole of precursors of 245fa (1233zd and 1234ze) and of products from the 240 series (243fa, 244fa and 245fa).

As for Example 14, the pressure was regulated at 20 bars and the temperature of the reactor was brought to 120°C for 5 and a half hours. After cooling to room temperature, the autoclave was completely degassed and the various phases collected were combined and washed with aqueous potassium hydroxide solution and with water.

The organic phase obtained no longer contained 1233zd and 1234ze and was composed of:

94% of 245fa

0.8% of 244fa

4.6% of 243fa.

CLAIMS

1. Process for the manufacture of 1,1,1,3,3-pentafluoropropane (245fa), which process comprises the liquid-phase catalytic fluorination of 1-chloro-3,3,3-trifluoropropene (1233zd) by means of anhydrous hydrofluoric acid.

2. Process according to Claim 1, in which the fluorination is carried out at a temperature of 50 to 150°C.

3. Process according to Claim 2, in which the fluorination temperature is between 80 and 140°C.

4. Process according to any one of the preceding Claims, in which the reaction is carried out batchwise under the autogenous pressure of the reaction mixture.

5. Process according to any one of Claims 1 to 3, in which the reaction is carried out continuously under a pressure of from 5 to 60 bars.

6. Process according to Claim 5, in which the pressure is between 10 and 40 bars.

7. Process according to Claim 5, in which the pressure is between 12 and 30 bars.

8. Process according to any one of the preceding Claims, in which the 1-chloro-3,3,3-trifluoropropene has been in a prior stage by gas-phase fluorination of 1,1,1,3,3-pentafluoropropane (240fa).

9. Process according to any one of Claims 1 to 7, in which there is used, as starting material, a

crude 1233zd containing minor amounts of 1,3,3,3-tetrafluoro-propene (1234ze), of 1,1-dichloro-3,3,3-trifluoropropane (243fa), of 1-chloro-1,3,3,3-tetrafluoropropane (244fa) and/or of 1,1,1,3,3-pentafluoropropane (245fa).

10. Process according to any one of the preceding Claims, in which the molar ratio of hydrofluoric acid to 1233zd, pure or crude, is between 2 and 30.

11. Process according to Claim 10, in which the molar ratio is between 3 and 15.

12. Process according to any one of the preceding Claims, in which the reaction is carried out in the presence of 0.005 to 0.05 mol of chlorine per mole of pure or crude 1233zd.

13. Process according to any one of the preceding Claims, in which the catalyst is a metal oxide, oxyhalide or halide.

14. Process according to Claim 13, in which the catalyst is a metal chloride, fluoride or chlorofluoride.

15. Process according to Claim 13, in which the catalyst is antimony pentachloride.

16. Process according to any one of the preceding Claims, in which 0.005 to 0.5 mol of catalyst are used per mole of organic product (pure or crude 1233zd).

17. Process according to Claim 16, in which

0.02 to 0.25 mol of catalyst are used.

18. Process for th manufacture of 1,1,1,3,3-pentafluoropropane substantially as described in any one of Examples 13 to 15.

19. 1,1,1,3,3-Pentafluoropropane obtained by the process claimed in any one of Claims 1 to 18.

20. Process for the manufacture of 1-chloro-3,3,3-trifluoropropene (1233zd), which process comprises the gas-phase treatment of a mixture of 1,1,1,3,3-pentachloropropane (240fa) and anhydrous hydrofluoric acid in the presence of a fluorination catalyst.

21. Process according to Claim 20, in which the reaction is carried out at a temperature of between 140 and 400°C.

22. Process according to Claim 21, in which the reaction temperature is between 180 and 350°C.

23. Process according to any one of Claims 20 to 22, in which the reaction is carried out under a pressure of between atmospheric pressure and 1.5 MPa.

24. Process according to any one of Claims 20 to 23, in which the contact time is between 0.5 and 100 seconds.

25. Process according to Claim 24, in which the contact time is between 2 and 30 seconds.

26. Process according to any one of Claims 20 to 25, in which the HF/240fa molar ratio is between 5 and 30.

27. Process according to any one of Claims 20 to 26, in which the reaction is carried out in the presence of 0.1 to 5 mol of oxygen or of chlorine per 100 mol of 240fa.

28. Process according to any one of Claims 20 to 27, in which there is used a catalyst based on chromium oxide, or a mixed catalyst containing chromium oxide and nickel fluoride.

29. Process for the manufacture of 1-chloro-3,3,3-trifluoropropene substantially as described in any one of Examples 1 to 12.

30. 1-Chloro-3,3,3-trifluoropropene obtained by the process claimed in any one of Claims 20 to 29.

31. Process for the manufacture of 1,1,1,3,3-pentafluoropropane (245fa) by the two stage fluorination of 1,1,1,3,3-pentachloropropane (240fa), which process comprises, in a first stage, the gas-phase treatment of a mixture of 1,1,1,3,3-pentachloropropane (240fa) and anhydrous hydrofluoric acid in the presence of a fluorination catalyst, and, in a second stage, the liquid-phase catalytic fluorination of the 1-chloro-3,3,3-trifluoropropene (1233zd) obtained in the first stage by means of anhydrous hydrofluoric acid.

32. Process according to Claim 31, in which the first stage is carried out under conditions as defined in any one of Claims 21 to 28, and the second stage is carried out under conditions as defined in any

one of Claims 2 to 16.

33. 1,1,1,3,3-Pentafluoropropane obtained by the process claimed in Claim 31 or 32.

The Patent Office

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Claims searched:	1-33	**Date of search:**	10 July 1997

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Databases searched:

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Other: Online: CAS ONLINE

Documents considered to be relevant:

Category	Identity of document and relevant passage		Relevant to claims
P,A	WO 97/15540 A1	(SOLVAY), 1 May 1997, see eg. claim 1	31 at least
A	EP 0703205 A1	(ELF ATOCHEM), see eg. claim 1	31 at least
P,X	US 5616819	(LAROCHE), 1 April 1997, see eg. claim 1	1 at least

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.